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INTRAMOLECULAR COORDINATION IN MOLECULES OF $C_6H_5COOCH_2CH_2SiX_3$ (X = F, Cl) *

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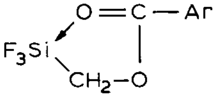
Summary

Silicon-substituted 2-benzoyloxyethylsilanes, $C_6H_5COOCH_2CH_2SiX_3$ with X = F, Cl, OCH_3 or $\frac{1}{3}(OCH_2CH_2)_3N$, have been synthesized for the first time. The molecules of compounds with X = F and Cl may exist in two forms, acyclic with a tetracoordinated silicon atom and cyclic with a six-membered ring and a pentacoordinated silicon atom.

The cyclic form of the molecules $C_6H_5COOCH_2CH_2SiX_3$, with X = F, Cl, are present in solutions of these compounds in non-polar solvents, the proportion increasing with decreasing temperature.

Results and discussion

At the present time, silicon compounds with an extended coordination sphere having no carbon analogs, are attracting ever increasing interest [1–3]. Earlier we have synthesized (aroyloxymethyl)trifluorosilanes (I) [4] with a pentacoordinate silicon atom and a five-membered ring closed by the intramolecular donor-acceptor Si←O bond.



(I)

At the same time, molecules of (3-benzoyloxypropyl)trifluorosilane, C_6H_5-

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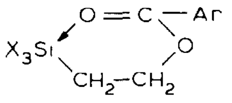
* The authers dedicate this paper to Prof. M. Kumada in recognition of his invaluable contributions to organosilicon chemistry in general, and to the chemistry of fluoro-substituted silicon compounds with an extended coordination number, in particular.

$COOCH_2CH_2CH_2SiF_3$ (II) display no intramolecular coordination between the silicon and oxygen [1]. These results inspired us to the synthesis of (2-benzoyloxyethyl)-trifluorosilane (III) and -trichlorosilane (IV), to examine the possibility of intramolecular coordination Si←O bond in their molecules resulting from six-membered ring closure, i.e., the possibility of the existence of these molecules in the form IIIa and IVa.



(IIIa, X = F,
IVa, X = Cl)

Compound III was synthesized according to equation 1. (2-Benzoyloxyethyl)tri-

$$C_6H_5COOCH{=}CH_2 + HSiCl_3 \rightarrow \underset{(IV)}{C_6H_5COOCH_2CH_2SiCl_3} \rightarrow \underset{(III)}{C_6H_5COOCH_2CH_2SiF_3} \qquad (1)$$

chlorosilane (IV) was obtained in 82% yield by the hydrosilylation of vinyl benzoate with trichlorosilane in the presence of Speier's catalyst. This compound was converted to compound III (in 70% yield) by treatment with 40% aqueous HF. An attempt to obtain (2-benzoyloxyethyl)trimethoxysilane (V), as the starting reagent for the synthesis of III, by treatment of (2-bromomethyl)trimethoxysilane with sodium benzoate in DMFA, was unsuccessful because β-cleavage occurred. Compound V is readily prepared, however, by the reaction of IV with methanol in the presence of urea. The reaction of V with HF also gives III.

(2-Benzoyloxyethyl)trifluorosilane (III) is a transparent odourless liquid, which can be distilled in vacuo, and this distinguishes this compound from organyltrifluorosilanes with a tetracoordinated silicon atom.

Compound III reacts with tris(2-trimethylsiloxyethyl)amine to form 1-(2′-benzoyloxyethyl)silatrane (VI) (in 84% yield) (eq. 2).

$$C_6H_5COOCH_2CH_2SiF_3 + \left[(CH_3)_3SiOCH_2CH_2\right]_3N \rightarrow \underset{(VI)}{C_6H_5COOCH_2CH_2Si(OCH_2CH_2)_3N} \qquad (2)$$

It was not possible to obtain VI by the conventional method [5], involving transetherification of (2-benzoyloxyethyl)trimethoxysilane (V) with tris(2-hydroxyethyl)amine, because β-cleavage occurs.

In order to establish the presence of the intramolecular coordinate Si ← O bond in compounds III and IV, i.e. the existence of these molecules in the forms IIIa and IVa, we have studied the IR spectra of solutions of these compounds in different solvents within the 173–298 K temperature range.

In the spectra of solutions of (2-benzoyloxyethyl)trifluorosilane in CH_2Cl_2 and CH_3CN the $\nu(C{=}O)$ stretching vibrations are represented by a single band at ~ 1720 cm^{-1} and this resembles the spectrum of $C_6H_5COO(CH_2)_3SiF_3$ (II) with a tetracoordinate silicon atom [1]. In the spectrum of a microfilm of III the bands related to the ν(C–O–C), ν_{as}(Si–F) and ν_s(Si–F) stretching vibrations are at 1272, 970 and 877 cm^{-1}, respectively. The spectra of solutions of III in non-polar solvents ($C_{10}H_{22}$ and

CCl_4) display a weak band at 1695 cm^{-1}, along with ν(C=O) bands at 1732 and 1729 cm^{-1}. With decreasing solution temperature, the intensity of the former increases, whereas that of the high-frequency band at ~ 1730 cm^{-1} drops. The spectrum of a frozen solution of III in $C_{10}H_{22}$ at 173 K shows, besides a band at 1690 cm^{-1}, weak bands at 1293 and 812 cm^{-1}. A similar picture is observed in the IR spectra of (aroyloxymethyl)trifluorosilanes with the intramolecular coordinated Si←O bond [1]. They exhibit a high-frequency displacement of the ν(C–O–C) band from 1272 cm^{-1} (in the spectrum of II) to 1356 cm^{-1}, and three bands of the SiF_3 group vibration, $\nu_{as}(SiF_{eq})$, $\nu_s(SiF_{eq})$ and $\nu(SiF_{ax})$ at 973, 873 and 817 cm^{-1}, respectively. These data show that the molecules of III in non-polar solvents are in both the acyclic form $C_6H_5COOCH_2CH_2SiF_3$, with a tetracoordinated silicon atom (IIIb), and the cyclic form (IIIa), with a pentacoordinated silicon atom. At 298 K the IIIa/IIIb equilibrium is strongly displaced to the IIIb form. A decrease in temperature of III in non-polar solvents displaces the equilibrium towards the form IIIa. The latter is also observed for III in CH_2Cl_2 at low temperatures (220–170 K). In CH_3CN, however, the molecules remain only in the acyclic form (IIIb) until the freezing point.

Similarly to compound III, (2-benzoyloxyethyl)trichlorosilane (IV) exists only in the acyclic form in polar solvent at 293 K. The spectrum of IV in heptane displays absorption bands (ν(C=O) 1733 cm^{-1}, ν(C–O–C) 1267 cm^{-1}, ν(SiCl) 598 and 576 cm^{-1}) which arise from the acyclic form. Apart from these bands, however, some weak absorption bands (ν(C=O) 1706 cm^{-1} and ν(Si–Cl) 460 cm^{-1}), which arise from the cyclic form IVa, with a pentacoordinated silicon atom, are also observed in this spectrum. As the solution temperature drops to the freezing point, the intensity of the above bands increases, which indicates the increasing dominance of the cyclic form of the molecules.

The possibility of intramolecular Si←O coordination in molecules of the type $C_6H_5COOCH_2CH_2SiX_3$ (X = F, Cl) suggests that there may also exist intramolecular Si←O coordination, i.e. involving a hexacoordinated silicon atom, in molecules of 1-(2′-benzoyloxyethyl)silatrane (VI). However the IR spectra of this compound both in solution and in the crystalline state have no specific features as compared with those of other 1-organylsilatranes [6].

The above experimental data and the results of our previous studies allow conclusions to be drawn about compounds in the series $C_6H_5COO(CH_2)_nSiF_3$. With $n = 1$ the compound has a pentacoordinated silicon atom and exists in a cyclic form (a five-membered ring closed by the intramolecular Si←O bond). This is the single structure for these molecules in non-polar and polar solvents, as well as in the crystalline and gaseous states up to 420 K. With $n = 2$, the six-membered cyclic form (extremely rare for intramolecular silicon complexes) with a pentacoordinated silicon atom exists only in non-polar media, in equilibrium with the acyclic form, the equilibrium being displaced towards the latter. The portion in the cyclic form increases with a decrease in the solution temperature. And, last, with $n = 3$, the molecules exist only in the acyclic form under the condition studied. This shows that no intramolecular coordination due to the Si←O closure of the seven-membered ring is observed.

One of the reasons for different ability of the compounds in the series $C_6H_5COO(CH_2)_nSiX_3$ (X = F) to form the intramolecular Si←O bond may be the unequal strain in the five-, six- and seven-membered rings with $n = 1$, 2 and 3, respectively. In our opinion, however, the most probable reason is the entropy control of intramolecular coordination. An entropy change becomes more prominant with increasing n due to an increase in the degrees of freedom of internal motion in the acyclic form.

Experimental

(2-Benzoyloxyethyl)trichlorosilane (IV). 29.6 g (0.2 mol) of vinyl benzoate and 0.15 ml of 0.05 M H_2PtCl_6 in isopropanol were placed in a three-necked flask equipped with a stirrer and a condenser, and then 27.1 g (0.2 mol) of $HSiCl_3$ was added dropwise. The reaction mixture was stirred at room temperature for 40 min and then heated to 155 °C. Unreacted vinyl benzoate was removed by distillation and the residue was distilled in vacuo to give 46.5 g of IV (82% yield), b.p. 130 °C (3 mmHg), n_D^{20} 1.5196, d_4^{20} 1.3289. Anal. Found: C, 39.59; H, 3.52; Si, 9.61; Cl, 36.53. $C_9H_9O_2SiCl_3$ calcd.: C, 38.06; H, 3.17; Si, 9.89; Cl, 37.53%.

(2-Benzoyloxyethyl)trifluorosilane (III). 6 ml of 40% aqueous HF (a two-fold excess) was added to 14.2 g (0.02 mol) of (benzoyloxyethyl)trichlorosilane in 10 ml of benzene. The mixture was stirred for 1 h, the upper layer was separated and dried over KF. After removal of the solvent, vacuum distillation of the residue yielded 8.2 g of III (70% yield), b.p. 77 °C (2 mmHg), n_D^{20} 1.4582, d_4^{20} 1.2831. Anal. Found: C, 47.32; H, 4.09; Si, 11.45; F, 24.06. $C_9H_9O_2SiF_3$ calcd.: C, 46.15; H, 3.08; Si, 12.00; F, 24.36%.

(2-Benzoyloxyethyl)trimethoxysilane (V). 9.4 g (0.03 mol) of (2-benzoyloxyethyl)trichlorosilane was added dropwise to a mixture of 6.0 g (0.03 mol) of urea, 3.2 g of dry CH_3OH and 20 ml of hexane. The mixture was stirred and heated for 2 h. After filtration and removal of the hexane, the residue was distilled in vacuo to give 7.3 g of V (81% yield), b.p. 150 °C (2 mmHg), n_D^{20} 1.4827, d_4^{20} 1.1374. Anal. Found: C, 53.36; H, 6.39; Si, 10.15. $C_{12}H_{18}O_5Si$ calcd.: C, 53.30; H, 6.66; Si, 10.37%.

1-(2'-Benzoyloxyethyl)silatrane (VI). A mixture of 2.3 g (0.01 mol) of (2-benzoyloxyethyl)trifluorosilane and 3.6 g (0.02 mol) of tris(trimethylsiloxyethyl)amine in 5 ml of benzene was heated for 30 min. Then benzene was removed and the precipitate was recrystallized from a chloroform/hexane mixture to give 2.7 g (84% yield) of VI, m.p. 135–137 °C. VI is soluble in benzene, acetonitrile and diethyl ether. Anal. Found: C, 55.01; H, 6.40; Si, 9.00. $C_{15}H_{21}O_5SiN$ calcd.: C, 55.72; H, 6.00; Si, 8.69%.

IR spectra of the compounds were recorded on a Specord 75 IR spectrophotometer. The concentrations of the solutions were about 0.10–0.01 mol l^{-1}. All the solvents were purified and dried by standard procedures.

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